

UC Irvine

UC Irvine Previously Published Works

Title

Effect of local and regional sources on the isotopic composition of nitrous oxide in the tropical free troposphere and tropopause layer

Permalink

<https://escholarship.org/uc/item/3vt4q83z>

Journal

Journal of Geophysical Research Atmospheres, 115(16)

ISSN

0148-0227

Authors

Croteau, P
Atlas, EL
Schauffler, SM
[et al.](#)

Publication Date

2010

DOI

10.1029/2009JD013117

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Effect of local and regional sources on the isotopic composition of nitrous oxide in the tropical free troposphere and tropopause layer

Philip Croteau,¹ Elliot L. Atlas,² Sue M. Schauffler,³ Donald R. Blake,⁴ Glenn S. Diskin,⁵ and Kristie A. Boering^{1,6}

Received 31 August 2009; revised 1 April 2010; accepted 7 April 2010; published 21 August 2010.

[1] Measurements and models of the spatiotemporal variability of surface N₂O mixing ratios and isotopic compositions are increasingly used to constrain the global N₂O budget. However, large variability observed on the small spatial scales of soil chambers and shipboard sampling, which appears to be very sensitive to local environmental conditions, has made extrapolation to the global scale difficult. In this study, we present measurements of the isotopic composition of N₂O ($\delta^{15}\text{N}^{\text{bulk}}$, $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$, and $\delta^{18}\text{O}$) from whole-air samples collected at altitudes of 0.5 to 19 km by the NASA DC-8 and WB-57 aircraft during the Costa Rica-Aura Validation Experiment (CR-AVE) and the Tropical Composition, Cloud and Climate Coupling Experiment (TC4) campaigns in January–February 2006 and July–August 2007, respectively. The vertical profiles of isotopic composition showed predictable, repeating patterns consistent with the influence of a surface source at lower altitudes and the influence of stratospheric photochemistry in the lower stratosphere. Their correlations with marine tracers at lower altitudes are consistent with a predominantly oceanic source, although a soil source cannot be ruled out. Measurements in a combustion plume revealed a strong depletion in ¹⁵N at the central nitrogen atom (i.e., low $\delta^{15}\text{N}^{\alpha}$ values), providing new information on N₂O isotopic compositions from combustion. This new data set demonstrates that a coherent picture of the isotopic composition of tropospheric N₂O is possible at currently attainable precisions and that its variations from 0.5 km to the lower stratosphere are a useful tool in investigating the sources and distributions of this important greenhouse gas.

Citation: Croteau, P., E. L. Atlas, S. M. Schauffler, D. R. Blake, G. S. Diskin, and K. A. Boering (2010), Effect of local and regional sources on the isotopic composition of nitrous oxide in the tropical free troposphere and tropopause layer, *J. Geophys. Res.*, 115, D00J11, doi:10.1029/2009JD013117.

1. Introduction

[2] Nitrous oxide, N₂O, is an important greenhouse gas with a tropospheric mixing ratio that has risen from a pre-industrial level of ~270 ppbv to current levels of ~320 ppbv [e.g., MacFarling-Meure *et al.*, 2006], revealing an imbalance between the N₂O sources and sinks of ~5 TgNyr^{−1} [Forster

et al., 2007]. The magnitudes of the particular processes that contribute to this imbalance (and how these may change as climate changes and as a side-effect of CO₂ mitigation strategies) have large uncertainties [e.g., Forster *et al.*, 2007]. Atmospheric N₂O originates predominantly at Earth's surface as a product or by-product of microbial nitrification and denitrification in water and in both natural and agricultural soils, and is emitted to the atmosphere by air-sea and air-soil exchange. These processes yield N₂O with oxygen and nitrogen isotopic compositions that depend on the isotopic composition of the N and O reservoirs from which it is produced as well as isotope effects associated with the microbiogeochemistry of N₂O production and consumption. The only major N₂O sink is destruction by photolysis and reaction with O(¹D) in the stratosphere, which enriches the remaining N₂O in the heavy isotopes ¹⁵N and ¹⁸O [e.g., Kim and Craig, 1993]. Since the sources and sinks of atmospheric N₂O determine its isotopic composition, isotope measurements can provide additional constraints on the N₂O budget beyond those based on measurements of N₂O mixing ratios alone

¹Department of Chemistry, University of California, Berkeley, Berkeley, California, USA.

²Division of Marine and Atmospheric Chemistry, University of Miami, Miami, Florida, USA.

³Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA.

⁴Department of Chemistry, University of California, Irvine, Irvine, California, USA.

⁵Chemistry and Dynamics Branch, NASA Langley Research Center, Hampton, Virginia, USA.

⁶Department of Earth and Planetary Science, University of California, Berkeley, Berkeley, California, USA.

[e.g., Kim and Craig, 1993; Toyoda et al., 2002; Park et al., 2004].

[3] So far, however, the large variability in N_2O isotopic compositions measured in and above soils [e.g., Pérez et al., 2000, 2001] and the oceans [e.g., Popp et al., 2002; Toyoda et al., 2002] has precluded a “bottom up” approach to simultaneously balancing the global N_2O concentration and isotope budgets. Isotopic compositions of emitted N_2O appear to depend sensitively on small-scale variations in many environmental parameters such as soil texture, soil water content, and substrate isotopic composition (e.g., nitrates), as well as the relative amounts of N_2O production (during nitrification and denitrification) and consumption (e.g., during denitrification under anaerobic conditions). Indeed, apportioning the relative amounts of N_2O production and consumption in the soils before emission to the atmosphere is one of the goals of using isotope measurements at the field scale [e.g., Bol et al., 2003; Pérez et al., 2006]; knowledge of how the magnitudes of these processes change with environmental variables could be used to adjust agricultural parameters, such as soil water content during fertilization, in order to mitigate the release of N_2O to the atmosphere and to better predict effective mitigation strategies as mean surface temperatures rise [e.g., Fujinuma and Balster, 2009; Baggs, 2008]. However, this large variability has also meant that a “bottom up” approach to balancing the regional, hemispheric, and global budgets is unlikely to be sufficiently constrained.

[4] A “top-down” approach via inverse modeling of N_2O measurements [Hirsch et al., 2006; Huang et al., 2008] has also been underconstrained, at least apart from box model studies of the long-term increase in N_2O concentrations and the concurrent depletion in its heavy isotopes that have been measured in air from firn and ice cores [Rahn and Wahlen, 2000; Sowers et al., 2002; Röckmann et al., 2003; Bernard et al., 2006; Ishijima et al., 2007]. Due to its long atmospheric lifetime of 120 years, N_2O (and hence its isotopic composition) has commonly been assumed to be well-mixed and thus was expected to show little variation in the troposphere, leaving inverse models underconstrained. Recently, however, time series analyses [Nevison et al., 2005, 2007; Jiang et al., 2007] of nearly continuous high-precision N_2O mixing ratio measurements at the surface have revealed detectable seasonal cycles and interannual variations in N_2O concentrations, and new N_2O isotope measurements on archived air samples from the surface at Cape Grim, Tasmania reveal the same [Park et al. 2005, 2008], demonstrating that a top-down approach using these data sets might ultimately help constrain the magnitudes of different sources. Further information on the isotopic compositions of N_2O emitted from the oceans and soils and the degree to which they may affect regional and hemispheric N_2O isotopic compositions are greatly needed to proceed, however, as there is a dearth of observations.

[5] Here, we report measurements of the ^{18}O and ^{15}N isotopic compositions (including site-specific ^{15}N) of N_2O in whole air samples collected from 0.5 km to the lower stratosphere in the tropics. The N_2O isotope altitude profiles obtained in both January and July in different years show a persistent pattern that, based on our initial analysis, appears to reflect the influence at lower altitudes of N_2O most likely from the ocean, transitioning at high altitudes in the lower

stratosphere to the influence of stratospheric photochemistry. Although the variations are small, they are detectable at current measurement precisions using Continuous-Flow Isotope Ratio Mass Spectrometry (CF-IRMS) and serve as the basis for hypotheses regarding the sources that control the isotopic composition of tropospheric nitrous oxide that we put forth here to be tested by future measurements and analyses. As such, these measurements, combined with future vertical profiles in different regions and with increased measurement precision, may finally succeed in allowing isotopes to be used in a “top down” approach to constrain the magnitude and distribution of anthropogenic and natural N_2O sources.

2. Methods

[6] Whole air samples were collected from the WB-57 aircraft in January and February 2006 during the Costa Rica-Aura Validation Experiment (CR-AVE) and from the WB-57 and DC-8 aircraft in July and August 2007 during the Tropical Composition, Cloud and Climate Coupling Experiment (TC4), both NASA missions based in San Jose, Costa Rica (9.99°N, 84.21°W). The University of Miami (UM) whole air sampler (WAS) [Flocke et al. 1999], which flew on the WB-57, included 50 1.5-L electropolished stainless steel canisters equipped with automated metal valves. The evacuated canisters were pressurized to 40 psi using a 4-stage bellows pump in flight. The University of California, Irvine (UCI) whole air sampler [Colman et al., 2001], which flew on the DC-8, used a stainless-steel bellows pump to pressurize 2-L stainless steel canisters to 40 psi. The canisters were equipped with stainless steel bellows valves and were evacuated and then filled with ~20 Torr of water vapor prior to the flights. Samples were collected in the planetary boundary layer, the free troposphere, and into the tropical tropopause layer (or “TTL,” defined here as the region between ~12–20 km [Toon et al., 2010], which includes the tropical lower stratosphere). Most of the WB-57 samples selected for isotopic analysis (see below) were collected between ~10 and 20 km, and those selected from among the DC-8 samples were collected between ~0.5 and 11.5 km. For reference, the cold-point tropopause was located on average at ~16.5 km during TC4 and ~17.5 km during CR-AVE. Most of the samples selected for isotopic analysis were collected between ~1°S and 10°N, but 25 of the samples were collected between ~20 and 30°N on two similar WB-57 transit flights (one for TC4 and one for CR-AVE) between Costa Rica and Houston, Texas. Sample selection was based largely on obtaining representative latitude and altitude distributions from both missions and on what samples were still available for analysis (i.e., those which had not been “recycled” to collect additional samples for trace gas analyses), with the exception of the plume samples which were selected because they were of interest based on the tracer mixing ratios.

[7] After sample collection, the WB-57 and the DC-8 whole air samples were first measured for numerous trace gas mixing ratios at UM and UCI, respectively, by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). For the WB-57 WAS samples, measurements that are relevant for this study are mixing ratios of N_2O , ethane

(C₂H₆), propane (C₃H₈), benzene (C₆H₆), and tetrachloroethylene (C₂Cl₄). In particular, N₂O mixing ratio measurements were made using an HP5890 II+ series GC fitted with an electron capture detector (ECD) relative to a 314 ppbv N₂O secondary standard of whole air calibrated against a National Institute of Standards and Technology (NIST) reference gas, Standard Reference Material #2608 with an N₂O mixing ratio of 300 nmol/mol ± 1%. The average uncertainty (2σ) for the N₂O mixing ratio data is less than 0.7 ± 1% [Hurst *et al.*, 2000]. Hydrocarbon species were measured by GC with flame ionization detection (GC-FID) with limits of detection (LOD) of about 2 ppt. C₂Cl₄ was measured with GC mass spectrometry (GC-MS) with LOD of better than 0.1 pptv. For the DC-8 samples, measurements that are relevant for this study include mixing ratios of methyl iodide (CH₃I), methyl nitrate (CH₃ONO₂), and ethyl nitrate (C₂H₅ONO₂), ethyne and benzene. CH₃I, CH₃ONO₂, and C₂H₅ONO₂ were measured by GC-ECD with LODs of 0.01, 0.02, and 0.02 pptv, respectively. Ethyne and benzene were measured by GC-FID, both with LODs of 3 pptv. Our analyses of the DC-8 samples also included correlations of the N₂O isotope measurements with in situ measurements of carbon monoxide (CO) and methane (CH₄) mixing ratios from a tunable diode laser instrument, DACOM [Sachse *et al.*, 1987, 1991]; measurements were made at 1 Hz with 0.1% precision and were averaged over the whole air canister sampling interval to compare with the whole air sample measurements. N₂O mixing ratio measurements sometimes made using the DACOM instrument are not available for these flights, nor were N₂O mixing ratios for the DC-8 samples measured at UCI. Since the ratio of the m/z 44 peak area of N₂O (measured on the IRMS at University of California at Berkeley (UCB)) to the sample pressure is proportional to the N₂O mixing ratio, we attempted to retrieve an N₂O mixing ratio from the IRMS data and the sample pressure at the time of the isotope analyses. However, because the pressure measurements during sample transfer from the canister to the IRMS flask (see below) were intended only as a house-keeping measure and not as an accurate absolute pressure measurement independent of the gaseous composition, a convection-enhanced pirani gauge that was not calibrated for samples of widely varying water content was used, and our attempt to retrieve a proxy for the N₂O mixing ratio of the sample was therefore not successful.

[8] After these and other trace gas mixing ratio measurements at UM and UCI, a total of 125 samples were selected for isotopic analysis and shipped to UCB. The isotopic composition of N₂O in the whole air samples was measured at UCB by CF-IRMS on a Finnigan MAT-252 coupled with preconcentration (PreCon) and gas chromatography (GC) devices – i.e., “PreCon/GC/CF-IRMS.” Prior to the isotope measurements, the CR-AVE whole-air samples were archived in 1.5-L Pyrex flasks; aliquots for the isotope measurements were taken from these archival flasks by expansion into evacuated 100–200 mL measurement flasks. The TC4 samples were not archived; 100 ml aliquots for isotope analysis were taken directly from the sample canisters.

[9] N₂O isotopic compositions are reported here as δ-values in “per mil” (‰), which is the part per thousand difference of the isotope ratio of the sample relative to a standard: $\delta = 1000 (R/R_{\text{standard}} - 1)$, where $R = {}^{15}\text{N}/{}^{14}\text{N}$ or ${}^{18}\text{O}/{}^{16}\text{O}$ and the

subscript ‘standard’ refers to an international reference material, which is air-N₂ for δ¹⁵N and Vienna Standard Mean Ocean Water (VSMOW) for δ¹⁸O. Two types of nitrogen isotopic compositions are reported: (1) δ¹⁵N^{bulk}, which is the ¹⁵N isotope composition averaged over the two nitrogen atom sites in N₂O, and (2) δ¹⁵N^α and δ¹⁵N^β, which represent the “site-specific” isotopic compositions – i.e., the ¹⁵N isotopic composition at the central nitrogen atom (the “α” site) and the ¹⁵N isotopic composition at the terminal nitrogen atom (the “β” site), respectively. In addition, we report the ‘Site Preference’ (SP) of the α-position relative to the β-position ($\text{SP} = {}^{15}\text{R}^{\alpha}/{}^{15}\text{R}^{\beta} - 1$), a form of the site-specific isotopic composition that is now frequently used, particularly in ecological studies in which it may be useful in discriminating between different production mechanisms [e.g., Bol *et al.*, 2003, Sutka *et al.*, 2006, Pérez *et al.*, 2006]. While some studies have used an alternative definition of SP as simply the difference between δ¹⁵N^α and δ¹⁵N^β values (i.e., $\text{SP} = \delta^{15}\text{N}^{\alpha} - \delta^{15}\text{N}^{\beta}$), a difference between truncated ratios is not a mathematically rigorous quantity [Gros *et al.*, 2003]. However, for the small values of SP usually encountered, the two expressions are equivalent [see, e.g., Toyoda *et al.*, 2004].

[10] Since the details of the isotopic measurements have been described elsewhere [Park *et al.*, 2004], only a brief overview is given here. Two aliquots are required to determine the site-specific isotopic composition of N₂O using the MAT-252 IRMS, one for δ¹⁵N^{bulk} and δ¹⁸O, and a second for δ¹⁵N^α and δ¹⁵N^β. To determine δ¹⁵N^{bulk} and δ¹⁸O values, m/z 44, 45, and 46 (which correspond to isotopologues of N₂O⁺) are measured and compared with a standard for the first aliquot. To determine δ¹⁵N^α, the NO⁺ fragment ion at m/z 30 and 31 is measured and compared with a standard for the second aliquot and the degree of ‘scrambling’ – i.e., the fraction of NO⁺ in the sample that included the β N-atom – is taken into account; the ‘scrambling factor’ measured for our Finnigan MAT-252 is 8.04% [see Kaiser *et al.*, 2004], which is similar to that measured for other 252 series instruments [e.g., Toyoda and Yoshida, 1999]. The measured values for δ¹⁵N^{bulk} and δ¹⁵N^α are then used to calculate δ¹⁵N^β, which in turn is combined with δ¹⁵N^α to calculate SP.

[11] Although for several years there had been controversy regarding how to convert δ¹⁵N^α and δ¹⁵N^β IRMS measurements onto the international air-N₂ scale [e.g., Toyoda and Yoshida, 1999; Yoshida and Toyoda, 2000; Kaiser *et al.* 2004; Park *et al.*, 2004; Westley *et al.* 2007], Griffith *et al.* [2009] recently determined the SP of tropospheric N₂O using a Fourier Transform infrared spectroscopic technique which is independent of mass spectrometric measurements, yielding values that are in agreement with the Yoshida and Toyoda [2000] air-N₂ scale. Thus, we report δ¹⁵N^α and δ¹⁵N^β values on the Yoshida and Toyoda [2000] scale using tropospheric N₂O as a ‘transfer standard’ given the SP value of tropospheric N₂O from Yoshida and Toyoda [2000] of 18.7‰, the value of δ¹⁵N^{bulk} of tropospheric N₂O measured at UCB of 6.2‰, and the measured site-specific isotopic composition relative to tropospheric N₂O at UCB to effect the conversion.

[12] The 1σ measurement precisions are ~0.2‰ for δ¹⁵N^{bulk}, 0.3‰ for δ¹⁸O, 0.8‰ for δ¹⁵N^α, and 0.9‰ for δ¹⁵N^β, determined by repeated measurements of different volumes of tropospheric air collected at UCB and by runs of

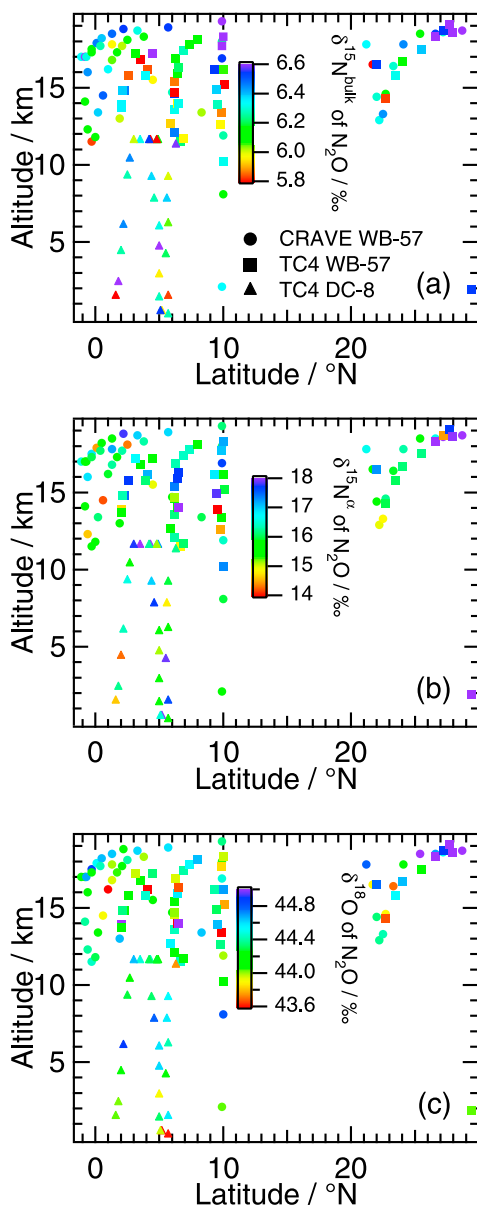


Figure 1. Whole air samples analyzed for the isotopic composition of N_2O for the CR-AVE and TC4 missions. Symbols show sampling location given by altitude (y axis) vs latitude (x axis) for the CR-AVE WB-57 samples (squares), TC4 WB-57 samples (triangles), and TC4 DC-8 samples (circles), color-scaled by the isotopic composition of N_2O : (a) $\delta^{15}\text{N}^{\text{bulk}}$, (b) $\delta^{15}\text{N}^{\alpha}$ and (c) $\delta^{18}\text{O}$. Aircraft landings in Costa Rica occurred at 10°N , while other descents occur as dives on various flights, as noted in the text.

a 1% N_2O -in-air laboratory standard [see, e.g., *Park et al.*, 2004; *Kaiser et al.*, 2003]. The precision is limited by instrumental noise, sample size, and the number of measurements for a given sample. In addition, the site-specific precisions are limited by the fact that two different aliquots are required for our MAT-252 since it is not possible to fit ion collectors for simultaneous measurements of m/z 30, 31, 44, 45, and 46 into the detection region. Of the 125 samples in this data set, 27 were measured in duplicate and showed repeatability that was similar to the precision. The accuracy

of the measurements reported here are estimated to be 1‰ for $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ and 4‰ for $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$ based on a comparison of the average isotopic composition of tropospheric N_2O reported by different groups, including ours, which show a range of differences of these magnitudes [*Yoshida and Toyoda*, 2000; *Kaiser et al.*, 2003; *Griffith et al.*, 2009]. Laboratory intercomparisons should improve the relative accuracies, and the implications of any future laboratory intercomparisons for the measurements reported here will be published when available.

3. Results and Discussion

[13] Figure 1 shows the latitude and altitude distribution of the 125 samples from CR-AVE and TC4 measured for N_2O isotopic compositions. Measured values for $\delta^{15}\text{N}^{\text{bulk}}$, $\delta^{15}\text{N}^{\alpha}$, and $\delta^{18}\text{O}$ are represented by the color scaling shown in the legends and are also given in Tables S1, S2, and S3.¹ As expected, the isotopic variability is small, with a range in δ -values for each equivalent to ~ 4 times the corresponding 1σ measurement precision, as is evident in the range of the legend. In the following sections, we examine both the averaged vertical profiles for the different aircraft and missions as well as unaveraged portions of particular flights that show interesting correlations with marine and combustion tracers. We focus on the tropical measurements ($<11^\circ\text{N}$) but include the subtropical points between 20° and 29°N in Figure 1 and the supplementary data files for completeness.

3.1. Averaged Vertical Profiles in the Tropics

[14] Figure 2 shows the results for averaging the tropical data (i.e., $<11^\circ\text{N}$) in 1-km altitude bins, parsed and color-coded by aircraft (WB-57 and DC-8) and campaign (CR-AVE and TC4). The error-bars shown are the 1σ standard deviation of the average of the data for that altitude bin (solid bars) or, for the few bins for which there is only a single datum, the measurement precision (dotted bars); the number of samples per altitude bin is also indicated in Figure 2a in the corresponding color. For comparison, the gray shading in each panel shows the $\pm 1\sigma$ ($N = 288$ for $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ and $N = 239$ for $\delta^{15}\text{N}^{\alpha}$) variability in measured tropospheric N_2O isotopic compositions in air sampled on the UCB campus (37.87°N , 122.26°W) between September 2001 and November 2006. (Note that the shaded ranges therefore include small trends and are thus larger than the day-to-day variability of tropospheric N_2O isotopic composition, which is similar to the measurement precision, suggesting no major influence from local sources. Furthermore, the meridional gradients between UCB and the tropics are expected to be well within these ranges [*Kaiser et al.*, 2003].)

[15] For $\delta^{15}\text{N}^{\text{bulk}}$, the average values and variability for the tropical profiles shown in Figure 2a fall within the range of those measured at the surface at midlatitudes at UCB. The largest deviation appears in the lower stratosphere, where average $\delta^{15}\text{N}^{\text{bulk}}$ values increase; this is shown more clearly in Figure 3 in which the measurements are binned into 0.5 km rather than 1 km ranges and then averaged. The

¹Auxiliary materials are available in the HTML. doi:10.1029/2009JD013117.

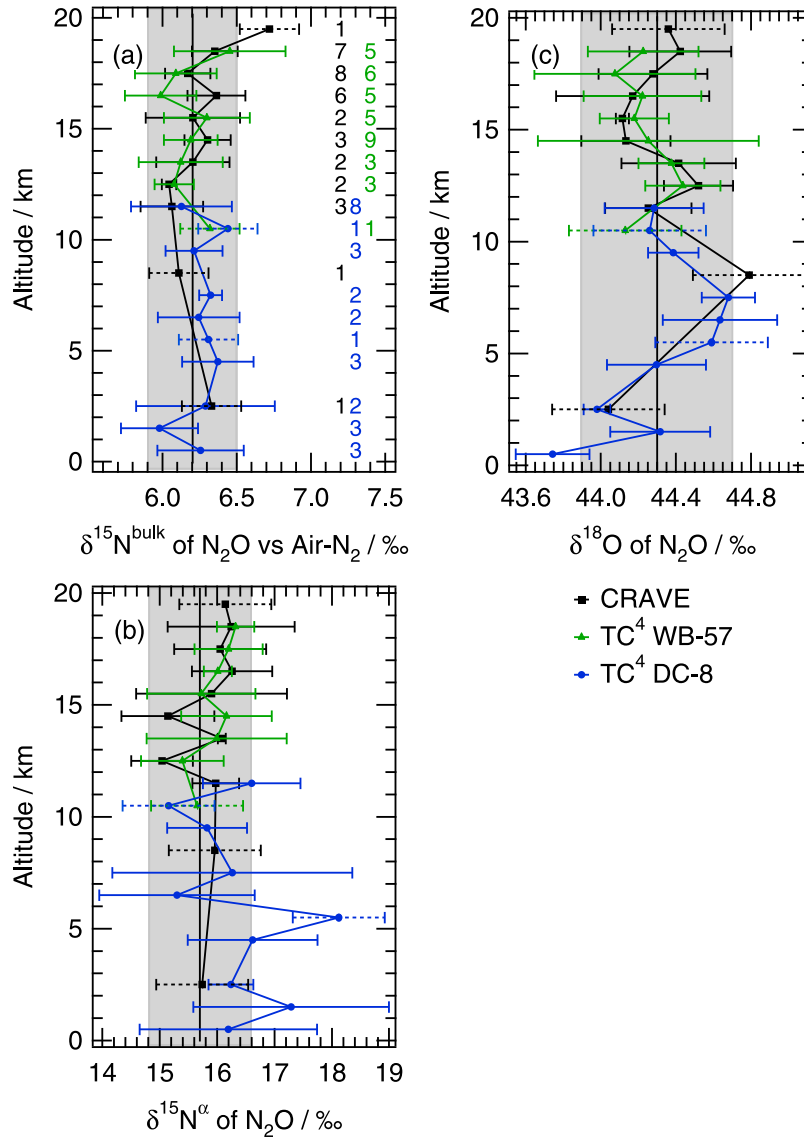


Figure 2. Vertical profiles of the isotopic composition of N_2O for samples collected at latitudes $< 11^\circ\text{N}$: (a) $\delta^{15}\text{N}^{\text{bulk}}$, (b) $\delta^{15}\text{N}^{\alpha}$, and (c) $\delta^{18}\text{O}$ for the CR-AVE WB-57 samples (circles), the TC4 WB-57 samples (triangles), and the TC4 DC-8 samples (squares). Measured values were binned and averaged in 1-km intervals. Error bars in each panel show the standard deviation of the mean for each bin, while the numbers in Figure 2a give the number of samples in each bin; bins for which there is only one sample are indicated by dashed error bars. For reference, the tropopause was located on average at ~ 16.5 km during TC4 and ~ 17.5 km during CR-AVE, as noted in the text.

increase in the $^{15}\text{N}/^{14}\text{N}$ ratio in N_2O with altitude is due primarily to the photolysis of N_2O in the stratosphere, which preferentially dissociates the $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ isotopologue with a smaller contribution from photo-oxidation of N_2O by reaction with $\text{O}(^1\text{D})$ [e.g., *Blake et al.*, 2003; *Johnson et al.*, 2001; *Kaiser et al.*, 2002a; *Yung and Miller*, 1997]. As the N_2O mixing ratios decrease with altitude in the stratosphere, the $\delta^{15}\text{N}^{\text{bulk}}$ values increase, as expected based on previous stratospheric measurements [e.g., *Toyoda et al.*, 2001; *Röckmann et al.*, 2001; *Park et al.*, 2004, *Kaiser et al.*, 2006].

[16] When the $\delta^{15}\text{N}^{\text{bulk}}$ and N_2O values for individual samples are plotted in a Rayleigh isotope fractionation format in Figure 4 (i.e., as $\ln(1 + \delta^{15}\text{N}^{\text{bulk}}/1000)$ vs $\ln([\text{N}_2\text{O}]/$

$[\text{N}_2\text{O}]_0$) where $[\text{N}_2\text{O}]_0$ is the N_2O mixing ratio for air entering the stratosphere) apparent fractionation constants, ε_{app} , of -21 ± 7 ‰ and -19 ± 7 ‰ are obtained for CR-AVE and TC4, respectively, from the slope of the fit line as determined by the Williamson-York method which considers uncertainty in both the x- and y-data [*Cantrell*, 2008, and references therein]. While the correlations are statistically significant ($R = -0.527$, $P < 0.03$ and $R = -0.610$, $P < 0.03$ for CR-AVE and TC4, respectively), the uncertainties are large since the N_2O mixing ratios decrease by only ~ 4 to 8 ppbv and the $\delta^{15}\text{N}^{\text{bulk}}$ values increase by only ~ 0.5 ‰ in the lowest 2 km of the stratosphere, which are intrinsically small and are close to the isotope measurement precision of ± 0.2 ‰. Nevertheless, these values for ε_{app} are within the

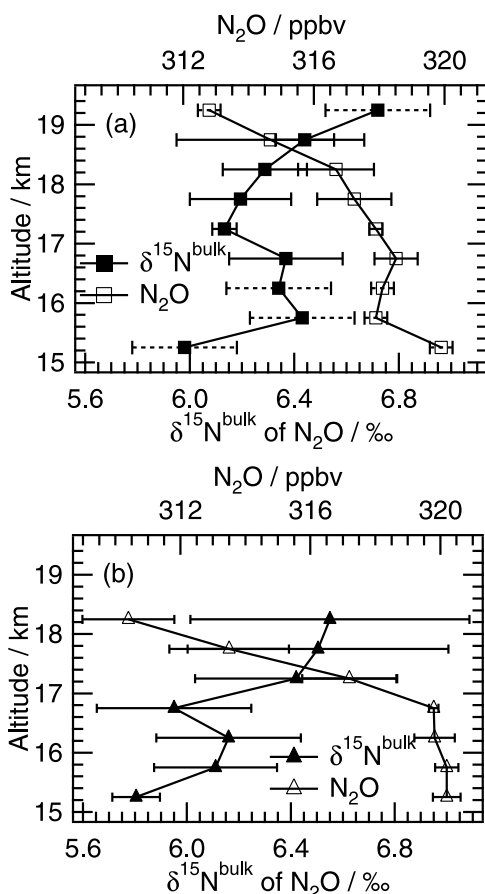


Figure 3. Vertical profiles of the mixing ratio (open symbols) and $\delta^{15}\text{N}^{\text{bulk}}$ (closed symbols) of N_2O , averaged into 0.5 km bins for samples collected at latitudes $< 11^\circ\text{N}$ and altitudes $> 15\text{km}$ for (a) CR-AVE and (b) TC4.

range of -14 to -19% obtained in the stratosphere for N_2O mixing ratios > 200 ppbv at 18°N [Kaiser et al., 2006], midlatitudes [e.g., Toyoda et al., 2001; Röckmann et al., 2001], and high latitudes [e.g., Park et al., 2004]. As discussed in the previous studies, these values for ϵ_{app} are at least a factor of two smaller than the fractionation constant expected in an isolated system – that is, one in which chemistry alone is acting to alter the isotopic composition and not transport or mixing of air of different isotopic compositions. For example, a value of -34.7% is expected based on broadband photolysis of N_2O at room temperature in the laboratory and a 10% contribution from N_2O oxidation by $\text{O}(^1\text{D})$ [Kaiser et al., 2002a; Röckmann et al., 2001]; transport and mixing decrease the slope of the Rayleigh fractionation line, yielding a value for ϵ_{app} that is necessarily smaller than that for an isolated system.

[17] This isotope fractionation cannot be due to in situ photochemistry in the lowest 2 km of the tropical stratosphere, however. The lifetime of N_2O at altitudes below 20 km in the tropics is ~ 70 years [e.g., Minschwaner et al., 1993]. Thus, on the time scales for tropical ascent, which require only about 4 months to ascend from 17 to 19 km [e.g., Eluszkiewicz et al., 1996; Rosenlof, 1995; Boering et al., 1996; Mote et al., 1996], N_2O mixing ratios should not decrease and N_2O should not become enriched in ^{15}N to the

extent observed by in situ photochemistry occurring in the tropics, as shown by a simple Rayleigh model analysis given in the appendix. Rather, as shown previously using measurements of the mixing ratios of a number of trace gas species below ~ 23 km, photochemically aged stratospheric air from midlatitudes must be transported and mixed isentropically into the tropical upwelling region [e.g., Avallone and Prather, 1996; Boering et al., 1996; Volk et al., 1996]; it is this mixing in of older midlatitude air rather than in situ N_2O destruction in the tropics that results in the decreasing N_2O mixing ratio and increasing ^{15}N enrichment with altitude above the tropical tropopause in Figure 3. In subsequent work, we will attempt to quantify this in-mixing of midlatitude air as a function of altitude and compare it with previous estimates based on the tracer mixing ratio models noted above since such a number is of interest for stratospheric dynamics, mean ages, and residence times and how these may or may not be changing over time [e.g., Engel et al., 2009; Austin and Li, 2006]. Finally, we note that an increase in $\delta^{18}\text{O}$ above the tropopause (e.g., Figure 2c) is not as clear as for $\delta^{15}\text{N}^{\text{bulk}}$ and not apparent at all in $\delta^{15}\text{N}^{\alpha}$ (e.g., Figure 2b); this difference with respect to $\delta^{15}\text{N}^{\text{bulk}}$ is likely due to a fractionation

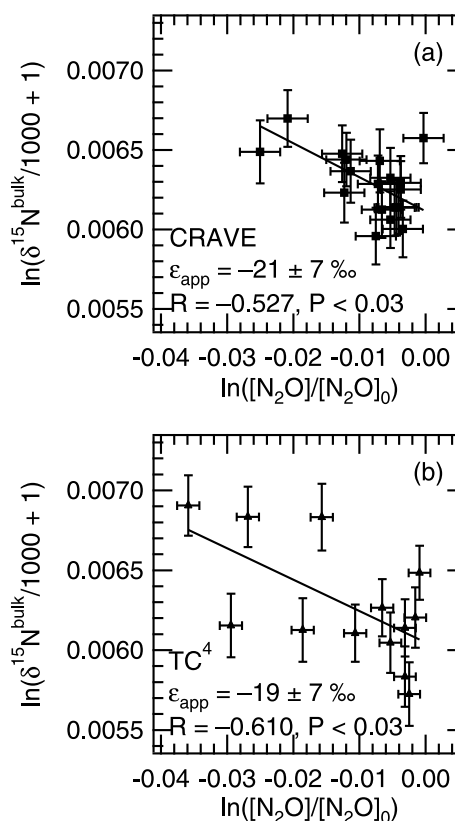


Figure 4. Individual measurements of $\delta^{15}\text{N}^{\text{bulk}}$ of N_2O for samples from the tropical lower stratosphere ($< 11^\circ\text{N}$ and (a) > 17 km for CR-AVE and (b) > 16 km for TC4) are shown here plotted in a Rayleigh isotope fractionation format, i.e., as $\ln(1 + \delta^{15}\text{N}^{\text{bulk}}/1000)$ vs $\ln([\text{N}_2\text{O}]/[\text{N}_2\text{O}]_0)$, where $[\text{N}_2\text{O}]_0$ is the N_2O mixing ratio for air entering the stratosphere, taken to be the average of the N_2O mixing ratios measured below the cutoff altitude, 319.4 ± 0.9 and 320.7 ± 0.4 for CR-AVE and TC4, respectively.

constant for $\delta^{18}\text{O}$ that is smaller than that for $\delta^{15}\text{N}^{\text{bulk}}$ by 10% and to a measurement precision that is 4 times larger for $\delta^{15}\text{N}^{\alpha}$ than for $\delta^{15}\text{N}^{\text{bulk}}$ so that stratospheric enrichments may be masked by noise in this data set.

[18] For $\delta^{18}\text{O}$, the averaged tropical profiles in Figure 2 show a remarkably consistent pattern between the CR-AVE and TC4 missions. At the lowest altitudes, N_2O is relatively depleted in ^{18}O , and is outside the $\pm 1\sigma$ range observed on average at the surface at UCB (gray shaded area). Values for $\delta^{18}\text{O}$ then increase up to ~ 8 or 9 km and then generally decrease up to the tropopause. Such repeatability between the two missions suggests that the profiles are determined by an interplay of similar processes. One possibility is that the drivers underlying this profile pattern are analogous to those for other species that exhibit a common “inverse C”-shaped altitude profile that is determined by convection of surface air combined with chemistry and/or mixing [e.g., *Prather and Jacob*, 1997]. For $\delta^{18}\text{O}$, an inverse C pattern could result from a source of N_2O that is depleted in ^{18}O relative to the free troposphere at the surface, either from soils or the ocean. Tropical convection takes this near-surface N_2O and deposits it at altitudes up to 10 to 14 km, thus leading to a decrease in $\delta^{18}\text{O}$ values at these higher altitudes influenced by convective outflow. In between these altitudes, the air may be more characteristic of background tropical and/or midlatitude air, with higher values of $\delta^{18}\text{O}$; the further from the surface source, the more it resembles background air (i.e., $\delta^{18}\text{O}$ increases with altitude) until convective outflow of surface air at higher altitudes begins to turn the profile back around toward lower $\delta^{18}\text{O}$ values. The vertical profiles for $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{15}\text{N}^{\alpha}$ (Figures 2a and 2b) do not show such a pattern.

[19] Comparing these characteristics of the vertical profiles for $\delta^{18}\text{O}$, $\delta^{15}\text{N}^{\text{bulk}}$, and $\delta^{15}\text{N}^{\alpha}$ with the range of isotopic compositions measured to date in soils and the ocean suggests that the source that may be influencing the lower altitudes may be more similar in isotopic composition to an ocean source than to a soil source, although a mixture of the two cannot be ruled out, particularly since both the Eastern Tropical North Pacific Ocean off the coast of Central America and tropical soils are thought to be significant sources of N_2O [e.g., *Cohen and Gordon*, 1978; *Nevison et al.*, 1995; *Matson and Vitousek*, 1990]. For example, the isotopic composition of N_2O in the subtropical North Pacific gyre was measured by *Popp et al.* [2002] and indicates that N_2O transferred from ocean to the air should be slightly depleted in bulk N and slightly more so in ^{18}O relative to the background troposphere; they suggest a range for the ocean source of 3.5 to 5.5‰ for $\delta^{15}\text{N}^{\text{bulk}}$ and 35.5 to 41.5‰ for $\delta^{18}\text{O}$. Different ranges for the isotopic composition of emitted N_2O have been measured in other ocean regions [e.g., *Toyoda et al.*, 2002]; in the absence of more comprehensive ocean measurements and an understanding of what controls them, the ranges relevant for this study will remain uncertain. In contrast, while there is great variability in measurements of the isotopic composition of N_2O emitted from soils, in general it is significantly more depleted in ^{15}N and ^{18}O relative to the tropospheric averages than an ocean source, and significantly more so in bulk ^{15}N than in ^{18}O . For example, the emission weighted isotope signature from unfertilized Costa Rican tropical rain forest soil $\delta^{15}\text{N}^{\text{bulk}} = -26 \pm 2.5\text{‰}$ and $\delta^{18}\text{O} = 26 \pm 6\text{‰}$ [*Pérez et al.*, 2000]. If a

soil source of N_2O were the dominant factor determining the lower $\delta^{18}\text{O}$ values in the lower altitudes of the vertical profile, then a signal in $\delta^{15}\text{N}^{\text{bulk}}$ would be expected to be even stronger and yet such behavior appears to be absent, as noted above. Furthermore, although measurements of the site-specific isotopic composition of oceanic N_2O are even more rare than $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$, *Toyoda et al.* [2002] have shown ocean profiles in which $\delta^{15}\text{N}^{\alpha}$ values are high and $\delta^{15}\text{N}^{\beta}$ are low relative to background tropospheric air; as a result, $\delta^{15}\text{N}^{\text{bulk}}$ values would be more similar to tropospheric air than either $\delta^{15}\text{N}^{\alpha}$ or $\delta^{15}\text{N}^{\beta}$ since it is the average of the two. Such a source could also be consistent with the observations since $\delta^{15}\text{N}^{\alpha}$ appears to be higher below 5 km, although such a pattern is arguably in the noise of the measurements. Overall, these characteristics of ocean N_2O isotopic compositions seem more similar to the trends and differences in the averaged profiles shown here than to a soil source, assuming the averaged profiles are indeed representative of regional profiles in general.

3.2. Correlations Between N_2O Isotopic Compositions and Surface Tracer Mixing Ratios

[20] Examining unaveraged measurements from the flight of 08 August 2007 for the TC4 mission may provide further insight into the possible influence of a surface source on the isotopic composition of N_2O in the tropical profiles. The DC-8 flight on this date included 3 distinct segments: a dive over the Pacific Ocean into the boundary layer, followed by an 11.5 km cruise and then a dive over the Colombian jungle. Particularly striking are the significant negative correlations between measurements of $\delta^{18}\text{O}$ of N_2O and the measured mixing ratios of methyl iodide (CH_3I), methyl nitrate (CH_3ONO_2), and ethyl nitrate ($\text{C}_2\text{H}_5\text{ONO}_2$), which are all tracers of marine convection, shown in Figure 5. While the correlations between $\delta^{18}\text{O}$ and the marine tracers for all 3 flight segments included together were significant ($P < 0.04$ for each marine tracer), inspection of the individual flight segments shows that the negative correlation is largely due to the Pacific dive. For the Pacific dive data, $R = -0.737$ and $P < 0.03$ for CH_3ONO_2 (Figure 5a), $R = -0.726$ and $P < 0.03$ for $\text{C}_2\text{H}_5\text{ONO}_2$ (Figure 5b), and $R = -0.714$ and $P < 0.04$ for CH_3I (Figure 5c) whereas the 2 other flight segments do not show statistically significant correlations ($P > 0.15$ for all). That these tracers of marine convection show a strong anti-correlation with $\delta^{18}\text{O}$, especially during the dive over the ocean, suggests that N_2O from the ocean may be influencing $\delta^{18}\text{O}$ of N_2O in the tropical profiles from both CR-AVE and TC4. Unfortunately, as noted above, the N_2O mixing ratios for these samples were not measured and, therefore, a Keeling plot analysis (in which the y-intercept of a plot of isotopic composition versus the reciprocal of the mixing ratio yields an estimate of the isotopic composition of the “undiluted” source [*Keeling*, 1958]) is impossible. Rather, the correlation with the marine tracers is only suggestive of an ocean link for the source, or at least one of the sources, influencing the decrease in $\delta^{18}\text{O}$ values toward the surface in the profiles shown here. For $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{15}\text{N}^{\alpha}$, the individual data points show no significant correlation with the marine tracers (see Figures S1 and S2).

[21] For samples from the descent over the Colombian jungle, $\delta^{18}\text{O}$ is significantly anti-correlated with the surface

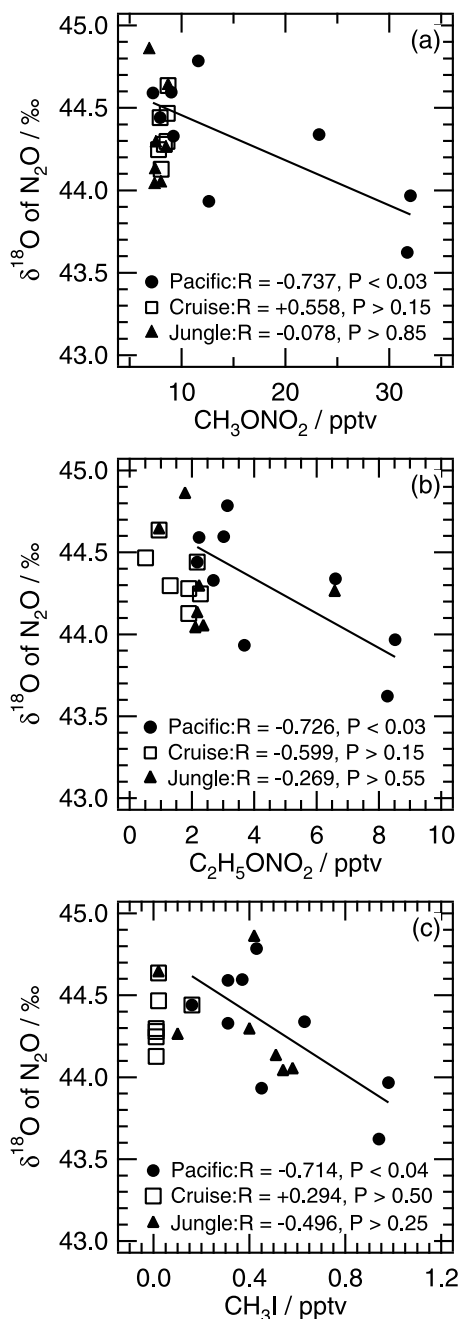


Figure 5. Tracer-tracer plots of $\delta^{18}\text{O}$ of N_2O vs mixing ratios of (a) CH_3ONO_2 , (b) $\text{C}_2\text{H}_5\text{ONO}_2$, and (c) CH_3I from the 08 August 2007 DC-8 samples, parsed into sections of the flight corresponding to a dive over the Pacific (circles; latitude = 4.3 to 5.2°N, longitude = 79.1 to 83.1°W, altitude = 0.5 to 11.6 km), a dive over the Colombian jungle (triangles; latitude = 1.6 to 3.0°N, longitude = 70.5 to 79.1°W, altitude = 1.5 to 11.6 km), and the DC-8 cruise region in between (squares; latitude = 3.4 to 4.3°N, longitude = 71.9 to 79.1°W, altitude = 11.6 km). The values of the correlation coefficient, R , are given in the figure legends, while the regression line shown is for the Pacific Ocean dive measurements.

tracers CO ($P < 0.02$) and ethyne ($P < 0.01$), which is consistent with either a soil or an ocean source since both are depleted in ^{18}O relative to background tropospheric N_2O ; see Figure S3. (We note that only 1 whole air sample from an altitude of 1.5 km for the jungle dive into the boundary layer was still available for isotopic analysis and it did not display the highly elevated isoprene mixing ratios of many of the other boundary layer samples taken at the bottom of the dive.) For $\delta^{15}\text{N}^{\text{bulk}}$, no significant correlation with surface tracers was observed ($P > 0.15$ for all), analogous to the lack of $\delta^{15}\text{N}^{\text{bulk}}$:marine tracer correlations for the ocean dive (Figure S1). Interestingly, however, there were significant positive correlations between $\delta^{15}\text{N}^{\alpha}$ and the surface tracers CH_4 ($P < 0.01$), ethyne ($P < 0.03$), and benzene ($P < 0.01$) in the jungle dive (Figure S2). Such a positive correlation is not expected for a soil source of N_2O . There are two interesting possibilities that might yield such positive correlations based on details of the flight. One is that the N_2O isotopic composition still reflects an ocean source (which is more likely to be enriched in ^{15}N at the α -position); back trajectory calculations by M. R. Schoeberl, P. A. Newman, and L. R. Lait (available through the NASA/ARC Earth Science Project Office Archive at <http://espoarchive.nasa.gov> [see also Schoeberl and Sparling, 1995]) suggest that the samples at 500 mbar pressure and lower altitudes had been over the Atlantic within 2 to 7 days of the flight. Another possibility is based on observations by the DC-8 whole air sampler scientist that at the bottom of the Colombian jungle dive there were a surprising number of swampy areas as well as cattle. Both are potential sources of N_2O enriched in ^{15}N at the α position relative to a soil source and, most likely, the background troposphere as well since in both systems N_2O may be reduced to N_2 during denitrification [Boontanon et al., 2000; Mahimairaja et al., 1995] which can cause ^{15}N accumulation in the remaining N_2O at the α position [e.g., Toyoda et al., 2005]. Given these two apparently plausible scenarios, it is unclear whether the positive correlations between $\delta^{15}\text{N}^{\alpha}$ and the surface tracers are rather local (as might be expected from cows and swamps) or more regional in nature (an ocean source, or a mixture of ocean and soil sources).

[22] In summary, the significant correlations observed between $\delta^{18}\text{O}$ and marine tracers from a dive over the Pacific Ocean suggest the influence of an ocean source on the N_2O isotopic composition in the lower tropical troposphere, while the correlations between $\delta^{18}\text{O}$ and $\delta^{15}\text{N}^{\alpha}$ and other surface tracers are consistent with the influence of either a continental and/or oceanic source. While more measurements are clearly needed to test the hypotheses put forth in this section, this new data set provides new constraints and points to specific needs for the further characterization of the isotopic composition of the various possible surface sources.

3.3. Isotopic Composition in a Combustion Plume

[23] Another flight yielding interesting correlations between the measured N_2O isotopic compositions and other atmospheric tracers was the WB-57 flight of 05 August 2007 from the TC4 mission. Samples from this flight yielded several measurements of site-specific N_2O isotopologues that showed a large deviation (4σ) from the average tropospheric values and a striking correlation with greatly

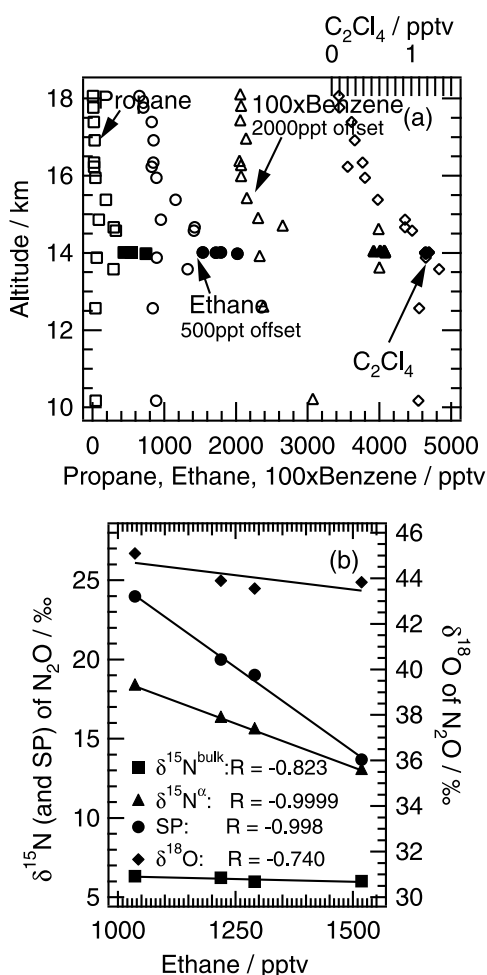


Figure 6. (a) Vertical profiles of the mixing ratios of propane (squares; in pptv), ethane (circles; in pptv and offset by 500 pptv), benzene (triangles; in 100 × pptv and offset by 2000 pptv), and tetrachloroethylene (C₂Cl₄, diamonds; in pptv, upper x axis) from the WB-57 flight of 05 August 2007; solid symbols show the samples designated here as being in the combustion plume at ~14 km altitude. (b) Correlation between the N₂O isotopic composition and the ethane mixing ratio for the combustion plume samples in Figure 6a (δ¹⁵N^{bulk}: squares; δ¹⁵N^α: triangles; Site Preference (see text): circles; and δ¹⁸O: diamonds).

enhanced mixing ratios of several tracers indicative of industrial combustion or biomass burning processes but only slightly enhanced N₂O mixing ratios of up to ~1 ppbv. The (unaveraged) altitude profiles for measurements of ethane, propane, benzene, and tetrachloroethylene are shown in Figure 6a. The plume, encountered at altitudes between 14 and 15 km is clearly visible. Trajectory-based convective influence calculations provided by L. Pfister [Pfister *et al.*, 2001, 2010] suggest that these samples were likely affected by convection within one day of the sampling, and that this convection was at least partially over Central America, near Panama City, Panama.

[24] Figure 6b shows the anti-correlation between δ¹⁵N^{bulk}, δ¹⁵N^α, Site Preference (the relative enrichment at

the α versus β nitrogen atom sites; see Methods), and δ¹⁸O of N₂O and the ethane mixing ratio for the 4 samples with the highest ethane mixing ratios. Values for δ¹⁵N^α and Site Preference are very strongly anti-correlated with ethane (R = -0.9999, P < 0.0003 and R = -0.998, P < 0.003, respectively). Such correlations are consistent with both expectations for and measurements of N₂O produced through biomass and fossil fuel combustion, which show that N₂O produced by combustion processes is depleted in ¹⁵N at the α nitrogen atom position relative to the β nitrogen atom position [Toyoda *et al.*, 2008; Ogawa and Yoshida, 2005a, 2005b], and we have found no evidence that the IRMS measurements may have been affected by spurious mass interferences in the polluted air. Because the N₂O mixing ratio in the plume samples varies by only 1 ppb or less against a background of 320 ppb, however, the isotopic composition of the source cannot be accurately quantified using a Keeling plot analysis (see, e.g., Pataki *et al.* [2003] in the context of CO₂). Overall, based on other tracers measured on the aircraft or in the samples, including CO, CO₂, particles, methyl chloride, methane, ethyne, and other non-methane hydrocarbons (not shown), and the fact that samples were collected directly in the outflow of a convective cloud, it is most likely that the plume represents a mixture of both urban pollution and biomass burning. To our knowledge, this is the first time that N₂O isotope measurements in such a plume influenced by combustion have been made in the remote atmosphere.

4. Conclusions

[25] We have demonstrated that the isotopic composition of nitrous oxide varies throughout the tropical troposphere with an average vertical structure in δ¹⁸O, discernible at current measurement precision, but that is not observed in the δ¹⁵N measurements – characteristics that are at least consistent with the influence of an oceanic source of N₂O on a regional scale, or perhaps a mixture of ocean and soil sources. This hypothesis is supported by correlations observed between δ¹⁸O of N₂O and tracers of marine convection, which are particularly strong during a dive over the Pacific Ocean. In addition, we have further demonstrated the dramatic effect of an industrial or biomass burning plume on the site-specific isotopic composition of N₂O. The hypotheses put forth here regarding the sources of N₂O and the extent of their regional and hemispheric influence on tropospheric profiles will require additional measurements to test them. On the other hand, we note that it is somewhat surprising that the variations in observed N₂O isotopic compositions and their coherent patterns with respect to altitude and the mixing ratios of a number of surface tracers is large enough to at least formulate the hypotheses put forth here. Nevertheless, the variations in the measurements of the isotopic composition of tropospheric N₂O reported here are small compared to the measurement precision – the range of measured isotopic compositions is only about 4σ – suggesting that improvements in analytical techniques (and/or using the more time-consuming dual inlet IRMS technique of Kaiser *et al.* [2003] or much larger samples sizes for many replicate CF-IRMS measurements on the same sample) would be useful, allowing more information to be extracted from the data. Ultimately, these measurements are “proof-of-

concept” that persistent and coherent variations in atmospheric N₂O isotopic compositions are measurable and could aid in using, e.g., inverse models to constrain the sources of N₂O on hemispheric to regional scales. Such modeling capabilities will be highly desirable not only for greenhouse gas concentration predictions and feedbacks but also for verification of future adherence to, e.g., Kyoto Protocol-like international agreements for N₂O emissions.

Appendix A

[26] Using the $\delta^{15}\text{N}^{\text{bulk}}$ measurements (shown in Figure 3), we can calculate a lower limit for the vertical ascent rate in the tropical lower stratosphere (TLS) during CR-AVE assuming no in-mixing of midlatitude air based on Rayleigh fractionation in an isolated system – i.e., by calculating how long it would take to enrich N₂O from the average $\delta^{15}\text{N}^{\text{bulk}}$ value observed at 17.25 km to that observed at 19.25 km based on the in situ destruction rate of N₂O. Using the fractionation constant of -34.7‰ noted above and a 70-year lifetime for N₂O with respect to photolysis yields an ascent rate of 0.063 mm s^{-1} (or 0.17 km/month), which implies that, if there were no in-mixing of midlatitude air, the air at 19.25 km would require 12 months to ascend to that altitude from 17.25 km in order to obtain the observed enrichment. In contrast, annually averaged vertical ascent rates in the TLS derived from observations of the propagation of annual cycles in CO₂ [Boering *et al.*, 1996] and water vapor [e.g., Mote *et al.*, 1996] and from radiative calculations [e.g., Eluszkiewicz *et al.*, 1996; Rosenlof, 1995] are $\sim 0.2 \text{ mm s}^{-1}$ ($\sim 0.5 \text{ km/month}$) and are even larger ($\sim 0.35 \text{ mm s}^{-1} = 0.88 \text{ km/month}$) during northern winter when the CR-AVE samples were collected, indicating that the transit time for air from ~ 17 to 19 km is on average 4 months, not 12 months, the value yielded by a Rayleigh model for an isolated lower stratosphere. Using temperature-dependent rather than room temperature photolysis fractionation constants, which gives an expected fractionation constant of -48 to -51‰ for the lower tropical stratosphere [Kaiser *et al.*, 2002a, 2002b], decreases that transit time to ~ 9 months, a time scale that is still more than a factor of two larger than the generally accepted ascent time scales noted above. Thus there is simply not enough time using a closed-system Rayleigh model to enrich tropical N₂O in ^{15}N to the extent observed by in situ photochemistry occurring in the tropics. Therefore, photochemically processed air that is isotopically enriched in ^{15}N must have mixed into the tropics, a conclusion that is consistent with the current understanding of the chemical composition of the TLS and the time scales for transport of older, midlatitude air into the tropics.

[27] **Acknowledgments.** We gratefully acknowledge support from the NASA Upper Atmosphere Research Program (NNG05G010G to UC Berkeley) and to U Miami, the NASA Tropospheric Chemistry Program, and a Camille Dreyfus Teacher-Scholar Award for K.A.B. We also thank R. Lueb for support in sample collection, Aaron Johnson for isotope measurements assistance, X. Zhu and L. Pope for laboratory work, G. Sachse and C. Harward for DACOM data, and L. Pfister of NASA Ames Research Center and M. Schoeberl, P. Newman, and L. Lait of the Atmospheric Chemistry and Dynamics Branch of the NASA Goddard Space Flight Center for convective influence and back trajectory calculations.

References

- Austin, J., and F. Li (2006), On the relationship between the strength of the Brewer-Dobson circulation and the age of stratospheric air, *Geophys. Res. Lett.*, **33**, L17807, doi:10.1029/2006GL026867.
- Avallone, L. M., and M. J. Prather (1996), Photochemical evolution of ozone in the lower tropical stratosphere, *J. Geophys. Res.*, **101**(D1), 1457–1461, doi:10.1029/95JD03010.
- Baggs, E. M. (2008), A review of stable isotope techniques for N₂O source partitioning in soils: Recent progress, remaining challenges and future considerations, *Rapid Commun. Mass Spectrom.*, **22**(11), 1664–1672, doi:10.1002/rcm.3456.
- Bernard, S., T. Röckmann, J. Kaiser, J.-M. Barnola, H. Fischer, T. Blunier, and J. Chappellaz (2006), Constraints on N₂O budget changes since pre-industrial time from new firn air and ice core isotope measurements, *Atmos. Chem. Phys.*, **6**, 493–503, doi:10.5194/acp-6-493-2006.
- Blake, G. A., M.-C. Liang, C. G. Morgan, and Y. L. Yung (2003), A Born-Oppenheimer photolysis model of N₂O fractionation, *Geophys. Res. Lett.*, **30**(12), 1656, doi:10.1029/2003GL016932.
- Boering, K. A., S. C. Wofsy, B. C. Daube, H. R. Schneider, M. Lowenstein, J. R. Podolske, and T. J. Conway (1996), Stratospheric mean ages and transport rates from observations of carbon dioxide and nitrous oxide, *Science*, **274**, 1340–1343, doi:10.1126/science.274.5291.1340.
- Bol, R., S. Toyoda, S. Yamulki, J. M. B. Hawkins, L. M. Cardenas, and N. Yoshida (2003), Dual isotope and isotopomer ratios of N₂O emitted from a temperate grassland soil after fertilizer application, *Rapid Commun. Mass Spectrom.*, **17**, 2550–2556, doi:10.1002/rcm.1223.
- Boontanon, N., S. Ueda, P. Kanatharana, and E. Wada (2000), Intramolecular stable isotope ratios of N₂O in the tropical swamp forest in Thailand, *Naturwissenschaften*, **87**, 188–192, doi:10.1007/s001140050701.
- Cantrell, C. A. (2008), Technical note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, *Atmos. Chem. Phys.*, **8**, 5477–5487, doi:10.5194/acp-8-5477-2008.
- Cohen, Y., and L. I. Gordon (1978), Nitrous oxide in the oxygen minimum of the eastern tropical North Pacific: Evidence for its consumption during denitrification and possible mechanisms for its production, *Deep Sea Res.*, **25**, 509–524, doi:10.1016/0146-6291(78)90640-9.
- Colman, J. J., A. L. Swanson, S. Meinardi, and D. R. Blake (2001), Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem.*, **73**, 3723–3731, doi:10.1021/ac010027g.
- Eluszkiewicz, J., D. Crisp, R. Zurek, L. Elson, E. Fishbein, J. Waters, R. G. Grainger, A. Lambert, R. Harwood, and G. Peckham (1996), Residual circulation in the stratosphere and mesosphere as diagnosed from Microwave Limb Sounder data, *J. Atmos. Sci.*, **53**(2), 217–240, doi:10.1175/1520-0469(1996)053<0217:RCITSA>2.0.CO;2.
- Engel, A., et al. (2009), Age of stratospheric air unchanged within uncertainties over the past 30 years, *Nat. Geosci.*, **2**(1), 28–31, doi:10.1038/ngeo388.
- Flocke, F., et al. (1999), An examination of chemistry and transport processes in the tropical lower stratosphere using observations of long-lived and short-lived compounds obtained during STRAT and POLARIS, *J. Geophys. Res.*, **104**(D21), 26,625–26,642, doi:10.1029/1999JD900504.
- Forster, P., et al. (2007), *Climate Change 2007: The Physical Science Basis*, edited by S. Solomon et al., Cambridge Univ. Press, Cambridge, U. K.
- Fujinuma, R., and N. J. Balster (2009), Using stable isotopes to reconcile the difference in nitrogen uptake efficiency relative to late season fertilization of northern red oak seedlings in Wisconsin bare-root nurseries, *Eos Trans. AGU*, **90**(52), Fall Meet. Suppl., Abstract B53B-0387.
- Griffith, D. W. T., S. D. Parkes, V. Haverd, C. Paton-Walsh, and S. R. Wilson (2009), Absolute calibration of the intramolecular site preference of ^{15}N fractionation in tropospheric N₂O by FT-IR spectroscopy, *Anal. Chem.*, **81**(6), 2227–2234, doi:10.1021/ac802371c.
- Gros, V., C. A. M. Brenninkmeijer, P. Jocke, J. Kaiser, D. Lowry, E. G. Nisbet, P. O'Brien, T. Röckmann, and N. Warwick (2003), Use of isotopes, in *Emissions of Atmospheric Trace Compounds*, *Adv. Global Change Res. Ser.*, vol. 18, edited by C. Granier, P. Artaxo, and C. E. Reeves, pp. 375–440, Springer, New York.
- Hirsch, A. I., A. M. Michalak, L. M. Bruhwiler, W. Peters, E. J. Dlugokencky, and P. P. Tans (2006), Inverse modeling estimates of the global nitrous oxide surface flux from 1998–2001, *Global Biogeochem. Cycles*, **20**, GB1008, doi:10.1029/2004GB002443.
- Huang, J., et al. (2008), Estimation of regional emissions of nitrous oxide from 1997 to 2005 using multinetwork measurements, a chemical transport model, and an inverse method, *J. Geophys. Res.*, **113**, D17313, doi:10.1029/2007JD009381.
- Hurst, D. F., et al. (2000), Construction of a unified, high-resolution nitrous oxide data set for ER-2 flights during SOLVE, *J. Geophys. Res.*, **105**(D15), 19,811–19,822, doi:10.1029/2000JD900218.

- Ishijima, K., S. Sugawara, K. Kawamura, G. Hashida, S. Morimoto, S. Murayama, S. Aoki, and T. Nakazawa (2007), Temporal variations of the atmospheric nitrous oxide concentration and its $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ for the latter half or the 20th century reconstructed from firm air analyses, *J. Geophys. Res.*, **112**, D03305, doi:10.1029/2006JD007208.
- Jiang, X., W. L. Ku, R.-L. Shia, Q. Li, J. W. Elkins, R. G. Prinn, and Y. L. Yung (2007), Seasonal cycle of N_2O : Analysis of data, *Global Biogeochem. Cycles*, **21**, GB1006, doi:10.1029/2006GB002691.
- Johnson, M. S., G. D. Billing, A. Groudis, and M. H. M. Janssen (2001), Photolysis of nitrous oxide isotopomers studied by time-dependent Hermite propagation, *J. Phys. Chem. A*, **105**, 8672–8680, doi:10.1021/jp011449x.
- Kaiser, J., C. A. M. Brenninkmeijer, and T. Röckmann (2002a), Intramolecular ^{15}N and ^{18}O fractionation in the reaction of N_2O with $\text{O}(^1\text{D})$ and its implications for the stratospheric N_2O isotope signature, *J. Geophys. Res.*, **107**(D14), 4214, doi:10.1029/2001JD001506.
- Kaiser, J., T. Röckmann, and C. A. M. Brenninkmeijer (2002b), Temperature dependence of isotope fractionation in N_2O photolysis, *Phys. Chem. Chem. Phys.*, **4**, 4420–4430, doi:10.1039/b204837j.
- Kaiser, J., T. Röckmann, and C. A. M. Brenninkmeijer (2003), Complete and accurate mass spectrometric isotope analysis of tropospheric nitrous oxide, *J. Geophys. Res.*, **108**(D15), 4476, doi:10.1029/2003JD003613.
- Kaiser, J., S. Park, K. A. Boering, C. A. M. Brenninkmeijer, A. Hilkert, and T. Röckmann (2004), Mass spectrometric method for the absolute calibration of the intramolecular nitrogen isotope distribution in nitrous oxide, *Anal. Bioanal. Chem.*, **378**, 256–269, doi:10.1007/s00216-003-2233-2.
- Kaiser, J., A. Engel, R. Borchers, and T. Röckmann (2006), Probing stratospheric transport and chemistry with new balloon and aircraft observations of the meridional and vertical N_2O distribution, *Atmos. Chem. Phys.*, **6**, 3535–3556, doi:10.5194/acp-6-3535-2006.
- Keeling, C. D. (1958), The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas, *Geochim. Cosmochim. Acta*, **13**, 322–334, doi:10.1016/0016-7037(58)90033-4.
- Kim, K.-R., and H. Craig (1993), Nitrogen-15 and oxygen-18 characteristics of nitrous oxide: A global perspective, *Science*, **262**, 1855–1857, doi:10.1126/science.262.5141.1855.
- MacFarling-Meure, C., D. M. Etheridge, C. M. Trudinger, L. P. Steele, R. L. Langenfelds, T. van Ommen, A. Smith, and J. W. Elkins (2006), Law Dome CO_2 , CH_4 , and N_2O ice core records extended to 2000 years BP, *Geophys. Res. Lett.*, **33**, L14810, doi:10.1029/2006GL026152.
- Mahimairaja, S., N. S. Bolan, and M. J. Hedley (1995), Denitrification losses of N from fresh and composted manures, *Soil Biol. Biochem.*, **27**(9), 1223–1225, doi:10.1016/0038-0717(95)00042-D.
- Matson, P. A., and P. M. Vitousek (1990), Ecosystem approach to a global nitrous oxide budget, *BioScience*, **40**(9), 667–672, doi:10.2307/1311434.
- Minschwaner, K., R. J. Salawitch, and M. B. McElroy (1993), Absorption of solar radiation by O_2 : Implications for O_3 and lifetimes of N_2O , CFCl_3 and CF_2Cl_2 , *J. Geophys. Res.*, **98**(D6), 10,543–10,561, doi:10.1029/93JD00223.
- Mote, P. W., K. H. Rosenlof, M. E. McIntyre, E. S. Carr, J. C. Gille, J. R. Holton, J. S. Kinnerson, H. C. Pumphrey, J. M. Russell III, and J. W. Waters (1996), An atmospheric tape recorder: The imprint of tropical tropopause temperatures on stratospheric water vapor, *J. Geophys. Res.*, **101**(D2), 3989–4006, doi:10.1029/95JD03422.
- Nevison, C. D., R. F. Weiss, and D. J. Erickson III (1995), Global oceanic emissions of nitrous oxide, *J. Geophys. Res.*, **100**(C8), 15,809–15,820, doi:10.1029/95JC00684.
- Nevison, C. D., R. F. Keeling, R. F. Weiss, B. N. Popp, X. Jin, P. J. Fraser, L. W. Porter, and P. G. Hess (2005), Southern ocean ventilation inferred from seasonal cycles of atmospheric N_2O and O_2/N_2 at Cape Grim, Tasmania, *Tellus, Ser. B*, **57**, 218–229.
- Nevison, C. D., N. M. Mahowald, R. F. Weiss, and R. G. Prinn (2007), Interannual and seasonal variability in atmospheric N_2O , *Global Biogeochem. Cycles*, **21**, GB3017, doi:10.1029/2006GB002755.
- Ogawa, M., and N. Yoshida (2005a), Intramolecular distribution of stable nitrogen and oxygen isotopes of nitrous oxide emitted during coal combustion, *Chemosphere*, **61**, 877–887, doi:10.1016/j.chemosphere.2005.04.096.
- Ogawa, M., and N. Yoshida (2005b), Nitrous oxide emission from the burning of agricultural residue, *Atmos. Environ.*, **39**, 3421–3429, doi:10.1016/j.atmosenv.2005.01.059.
- Park, S., E. L. Atlas, and K. A. Boering (2004), Measurements of N_2O isotopologues in the stratosphere: Influence of transport on the apparent enrichment factors and the isotopologue fluxes to the troposphere, *J. Geophys. Res.*, **109**, D01305, doi:10.1029/2003JD003731.
- Park, S., K. A. Boering, D. M. Etheridge, D. Forrester, K.-R. Kim, R. L. Langenfelds, T. van Ommen, L. P. Steele, and C. M. Trudinger (2005), Trends in the nitrogen and oxygen isotopic compositions of tropospheric nitrous oxide and implications for the global budget, *Eos Trans. AGU*, **86**(52), Abstract A44B-03.
- Park, S., et al. (2008), Trends, seasonal cycles, and interannual variability in the isotopic composition of nitrous oxide between 1940 and 2008, *Eos Trans. AGU*, **89**(53), Abstract A21A-0125.
- Pataki, D. E., J. R. Ehleringer, L. B. Flanagan, D. Yakir, D. R. Bowling, C. J. Still, N. Buchmann, J. O. Kaplan, and J. A. Berry (2003), The application and interpretation of Keeling plots in terrestrial carbon cycle research, *Global Biogeochem. Cycles*, **17**(1), 1022, doi:10.1029/2001GB001850.
- Pérez, T., S. E. Trumbore, S. C. Tyler, E. A. Davidson, M. Keller, and P. B. de Camargo (2000), Isotopic variability of N_2O emissions from tropical forest soils, *Global Biogeochem. Cycles*, **14**(2), 525–535, doi:10.1029/1999GB001181.
- Pérez, T., S. E. Trumbore, S. C. Tyler, P. A. Matson, I. Ortiz-Monasterio, T. Rahn, and D. W. T. Griffith (2001), Identifying the agricultural imprint on the global N_2O budget using stable isotopes, *J. Geophys. Res.*, **106**(D9), 9869–9878, doi:10.1029/2000JD900809.
- Pérez, T., D. Garcia-Montiel, S. Trumbore, S. Tyler, P. de Camargo, M. Moriera, M. Piccolo, and C. Cerri (2006), Nitrous oxide nitrification and denitrification ^{15}N enrichment factors from Amazon forest soils, *Ecol. Appl.*, **16**(6), 2153–2167, doi:10.1890/1051-0761(2006)016[2153:NONADN]2.0.CO;2.
- Pfister, L., et al. (2001), Aircraft observations of thin cirrus clouds near the tropical tropopause, *J. Geophys. Res.*, **106**(D9), 9765–9786, doi:10.1029/2000JD900648.
- Pfister, L., H. B. Selkirk, D. O. Starr, K. H. Rosenlof, and P. A. Newman (2010), A meteorological overview of the TC4 mission, doi:10.1029/2009JD013316, in press.
- Popp, B. N., et al. (2002), Nitrogen and oxygen isotopomeric constraints on the origins and sea-to-air flux of N_2O in the oligotrophic subtropical North Pacific gyre, *Global Biogeochem. Cycles*, **16**(4), 1064, doi:10.1029/2001GB001806.
- Prather, M. J., and D. J. Jacob (1997), A persistent imbalance in HO_x and NO_x photochemistry of the upper troposphere driven by deep tropical convection, *Geophys. Res. Lett.*, **24**(24), 3189–3192, doi:10.1029/97GL03027.
- Rahn, T., and M. Wahlen (2000), A reassessment of the global budget of atmospheric nitrous oxide, *Global Biogeochem. Cycles*, **14**(2), 537–543, doi:10.1029/1999GB900070.
- Röckmann, T., J. Kaiser, and C. A. M. Brenninkmeijer (2003), The isotopic fingerprint of the pre-industrial and the anthropogenic N_2O source, *Atmos. Chem. Phys.*, **3**, 315–323.
- Röckmann, T., J. Kaiser, C. A. M. Brenninkmeijer, J. N. Crowley, R. Borchers, W. A. Brand, and P. J. Crutzen (2001), Isotopic enrichment of nitrous oxide ($^{15}\text{N}^{14}\text{NO}$, $^{14}\text{N}^{15}\text{NO}$, $^{14}\text{N}^{14}\text{N}^{18}\text{O}$) in the stratosphere and in the laboratory, *J. Geophys. Res.*, **106**(D10), 10,403–10,410, doi:10.1029/2000JD900822.
- Rosenlof, K. H. (1995), Seasonal cycle of the residual mean meridional circulation in the stratosphere, *J. Geophys. Res.*, **100**(D3), 5173–5191, doi:10.1029/94JD03122.
- Sachse, G. W., G. F. Hill, L. O. Wade, and M. G. Perry (1987), Fast-response, high precision carbon monoxide sensor using a tunable diode laser absorption technique, *J. Geophys. Res.*, **92**, 2071–2081, doi:10.1029/JD092iD02p02071.
- Sachse, G. W., J. E. Collins, G. F. Hill, L. O. Wade, L. G. Burney, and J. A. Ritter (1991), Airborne tunable diode laser sensor for high precision concentration and flux measurements of carbon monoxide and methane, *Proc. SPIE Int. Opt. Eng.*, **1433**, 145–156.
- Schoeberl, M. R., and L. Sparling (1995), Trajectory modeling, in *Diagnostic Tools in Atmospheric Physics, Proc. Int. School Phys. "Enrico Fermi,"* vol. 124, edited by G. Fiocco and G. Visconti, pp. 289–306, IOS Press, Amsterdam.
- Sowers, T., A. Rodenbaugh, N. Yoshida, and S. Toyoda (2002), Extending the records of the isotopic composition of atmospheric N_2O back to 1800 A.D. from firm air trapped in snow at the South Pole and the Greenland Ice Sheet Project II ice core, *Global Biogeochem. Cycles*, **16**(4), 1129, doi:10.1029/2002GB001911.
- Sutka, R. L., N. E. Ostrom, P. H. Ostrom, J. A. Breznak, H. Gandhi, A. J. Pitt, and F. Li (2006), Distinguishing nitrous oxide production from nitrification and denitrification on the basis of isotopomer abundances, *Appl. Environ. Microbiol.*, **72**(1), 638–644, doi:10.1128/AEM.72.1.638-644.2006.
- Toon, O. B., et al. (2010), Planning, implementation and first results of the Tropical Composition, Cloud and Climate Coupling Experiment (TC4), *J. Geophys. Res.*, **115**, D00J04, doi:10.1029/2009JD013073.
- Toyoda, S., and N. Yoshida (1999), Determination of nitrogen isotopomers of nitrous oxide on a modified isotope ratio mass spectrometer, *Anal. Chem.*, **71**, 4711–4718, doi:10.1021/ac9904563.

- Toyoda, S., N. Yoshida, T. Urabe, S. Aoki, T. Nakazawa, S. Sugawara, and H. Honda (2001), Fractionation of N_2O isotopomers in the stratosphere, *J. Geophys. Res.*, **106**(D7), 7515–7522, doi:10.1029/2000JD900680.
- Toyoda, S., N. Yoshida, T. Miwa, Y. Matsui, H. Yamagishi, U. Tsunogai, Y. Niojiri, and N. Tsurushima (2002), Production mechanism and global budget of N_2O inferred from its isotopomers in the western North Pacific, *Geophys. Res. Lett.*, **29**(3), 1037, doi:10.1029/2001GL014311.
- Toyoda, S., et al. (2004), Temporal and latitudinal distributions of stratospheric N_2O isotopomers, *J. Geophys. Res.*, **109**, D08308, doi:10.1029/2003JD004316.
- Toyoda, S., H. Mutoke, H. Yamagishi, N. Yoshida, and Y. Tanji (2005), Fractionation of N_2O isotopomers during production by denitrifier, *Soil Biol. Biochem.*, **37**, 1535–1545, doi:10.1016/j.soilbio.2005.01.009.
- Toyoda, S., S.-I. Yamamoto, S. Arai, H. Nara, N. Yoshida, K. Kashiwakura, and K.-I. Akiyama (2008), Isotopomeric characterization of N_2O produced, consumed, and emitted by automobiles, *Rapid Commun. Mass Spectrom.*, **22**, 603–612, doi:10.1002/rcm.3400.
- Volk, C. M., et al. (1996), Quantifying transport between the tropical and mid-latitude lower stratosphere, *Science*, **272**, 1763–1768, doi:10.1126/science.272.5269.1763.
- Westley, M. B., B. N. Popp, and T. M. Rust (2007), The calibration of the intramolecular nitrogen isotope distribution in nitrous oxide measured by isotope ratio mass spectrometry, *Rapid Commun. Mass Spectrom.*, **21**, 391–405, doi:10.1002/rcm.2828.
- Yoshida, N., and S. Toyoda (2000), Constraining the atmospheric N_2O budget from intramolecular site preference in N_2O isotopomers, *Nature*, **405**, 330–334, doi:10.1038/35012558.
- Yung, Y. L., and C. E. Miller (1997), Isotopic fractionation of stratospheric nitrous oxide, *Science*, **278**, 1778–1780, doi:10.1126/science.278.5344.1778.
- E. L. Atlas, Division of Marine and Atmospheric Chemistry, University of Miami, Miami, FL 33149, USA.
- D. R. Blake, Department of Chemistry, University of California, Irvine, CA 92697–2025, USA.
- K. A. Boering and P. Croteau, Department of Chemistry, University of California, Berkeley, CA 94720, USA.
- G. S. Diskin, Chemistry and Dynamics Branch, NASA Langley Research Center, Hampton, VA 23681, USA.
- S. M. Schauffler, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80307–3000, USA.